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NMR evidence for Co–Al–Co molecular groups trapped in cages of Co_4Al_{13}

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ABSTRACT

We present the results of ^{27}Al nuclear magnetic resonance (NMR) experiments on the phase Co_4Al_{13}. These results are compared to a recent structure model [1], which demonstrates a unique bonding for Al atoms in the Co–Al–Co molecular groups. In our measurement, two ^{27}Al signals were identified. The first one originates from Al atoms forming cages. The second signal corresponds to Al sites with exceptionally large almost axially symmetric quadrupole coupling. This finding is in perfect agreement with isolated Co–Al–Co molecular groups in accordance to Ref. [1].

1. Introduction

The orthorhombic phase Co_4Al_{13}, which features 102 atoms per unit cell, atomic cluster arrangements and inherent disorder [2], is considered as a complex metallic alloy [3]. Furthermore, possessing a layered structure and pentagonal channels [2], it is a decagonal quasicrystal approximant [4]. Recent X-ray investigation in combination with an analysis of the chemical bonding based on quantum mechanical calculations revealed the structural resemblance of Co_4Al_{13} and clathrates [1]. Co–Al–Co molecular groups are considered as guests trapped in cages formed by other Al and Co atoms. According to this model a unique bonding situation for the Al atoms in the Co–Al–Co molecular groups in comparison with the other Al atoms is expected. Since NMR as a local probe has been proven to give insight into the local arrangements of the atoms of intermetallic compounds [5,6], ^{27}Al NMR measurements on powder samples and a single-crystal were done to get independent support for this model.

2. Experimental

In our study a single-crystal with a nominal composition $Co_{24}Al_{76}$ was used. It was grown by means of the Bridgman method. In order to perform crystalline-direction-dependent NMR studies, a bar-shaped sample of dimensions 1 mm × 1 mm × 2 mm was cut from the crystal, with all faces perpendicular to main crystalline axes. A part of the same ingot was pulverized to obtain powder sample of Co_4Al_{13}.

The ^{27}Al NMR experiments (spin $I = 5/2$) were performed at ambient temperature using Bruker AVANCE and TecMag Apollo spectrometers with magnetic fields of 11.74 T and 7.05 T, respectively. The corresponding reference frequencies of $Al(NO_3)_3$ were 130.32 MHz and 78.21 MHz. In all presented experiments a solid echo sequence with both pulses of 1.5 μs duration and an interpulse delay of 30 μs was used. Repetition time was 0.25 s. The electric quadrupole interaction is determined by the quadrupole coupling constant defined as $\nu_Q = 3e^2qQ/20h$ for spin $I = 5/2$, and by the asymmetry parameter $\eta = (V_{xx} - V_{yy})/V_{zz}$ [7].

3. Results and discussion

The powder spectrum of the ^{27}Al central transition measured at magnetic fields of 11.74 T and 7.05 T shows a featureless main contribution (A) that belongs to the majority of chemically non-equivalent Al sites (Fig. 1a and c). An increase of the signal width in the low magnetic field compared to the high magnetic field indicates that signal (A) is dominated by quadrupole coupling. An additional signal contribution (B) appears at higher frequency and seems to be clearly separated from the main contribution (A) using

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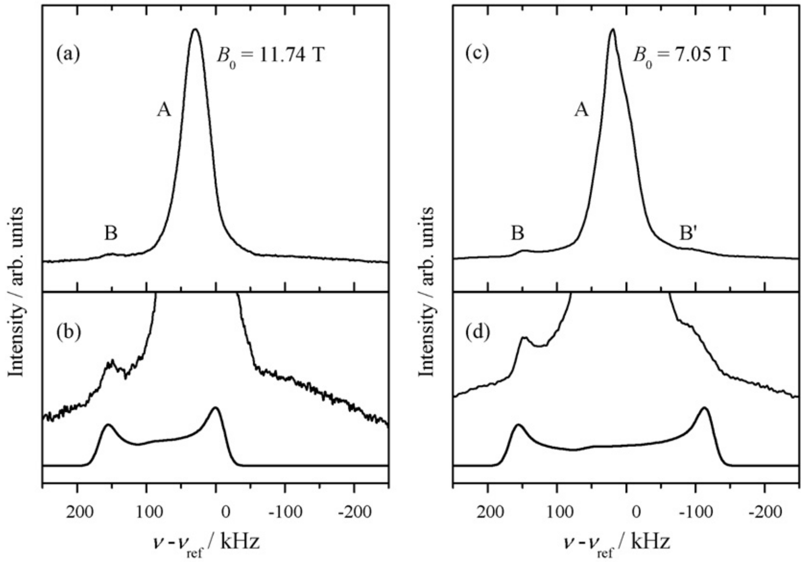

Fig. 1. (a) ^{27}Al NMR lineshape of the central transition in the magnetic field $B_0 = 11.74$ T for a powder sample of Co_4Al_{13}. (b) Enlarged section of (a) together with a simulated spectrum with $\nu_Q = 4.0$ MHz, $\eta = 0$ and $\delta_{iso} = 780$ ppm. The graphs (c) and (d) show corresponding ^{27}Al NMR lineshape in the magnetic field $B_0 = 7.05$ T. Label A indicates the main contribution, B and B' the additional signal contributions.

$B_0 = 11.74$ T (Fig. 1a). A similar feature is visible in the low field spectrum (Fig. 1c), where an additional signal contribution (B') appears at lower frequencies being also separated from the main signal (A).

To understand the origin of the separated signal contributions B and B', the angular dependence of the NMR lineshape with axes of rotation parallel to [1 0 0], [0 1 0] and [0 0 1] directions of a single-crystal Co_4Al_{13} was measured in the magnetic field $B_0 = 11.74$ T (axis of rotation was always perpendicular to the magnetic field). The usage of a single-crystal results in a much higher resolution and allows the study of the angular dependence for different signal contributions separately. The signal contribution (B) is angular independent for rotation around the [1 0 0] axis (Fig. 2a), whereas it exhibits a strong angular dependence for rotation around the [0 0 1] axis (Fig. 2b). Rotation around the [0 1 0] axis has similar pattern as rotation around the [0 0 1] axis. Therefore, the shift tensor or/and the electric field gradient (EFG) tensor should be almost axially symmetric ($\eta \approx 0$) with the largest principal eigenvector pointing along the [1 0 0] direction. The calculated pattern for rotation around the [0 0 1] (assuming axially symmetric tensor along the [1 0 0] direction), has the following functional forms, $\nu = A_1 + A_2 \cos 2\alpha$ and $\nu = B_1 + B_2 \cos 2\alpha + B_3 \cos 4\alpha$, for shift anisotropy and electric quadrupole interaction, respectively [6,7]. Only the second functional form describes the measured rotation patterns of the signal contribution (B) correctly, which is a proof that electric quadrupole interaction is mainly responsible for the observed angular dependence. From simulations of the rotation patterns for signal (B) (solid lines in Fig. 2), the quadrupole coupling constant $\nu_Q \approx 4.0$ MHz, the asymmetry parameter $\eta \approx 0$ and the isotropic shift $\delta_{iso} \approx 780$ ppm, were estimated. More precise measurements with higher angular resolution are necessary in order to determine the influence of the quadrupole coupling and the shift parameters, especially the expected shift anisotropy, quantitatively.

The main signal contribution (A) is determined by sites with much lower values of quadrupole coupling not exceeding $\nu_Q \approx 1.5$ MHz, asymmetry parameter η ranging from 0 to 1, and a broad distribution of isotropic shift centred at $\delta_{iso} \approx 300$ ppm. These values were obtained by simulations of powder spectra, frequency-sweep experiments and ^{27}Al triple-quantum magic-angle spinning NMR experiments. The simulated powder lineshape of the signal (B) is partially hidden by the main contribution (A) in high magnetic field (Fig. 1b), whereas it is resolved in the low magnetic field (Fig. 1d), appearing as signal contributions (B) and (B'). An additional proof of this model was a confirmation of satellite transitions obtained by a frequency-sweep experiment for a single-crystal sample, which is in agreement with $\nu_Q \approx 4.0$ MHz.

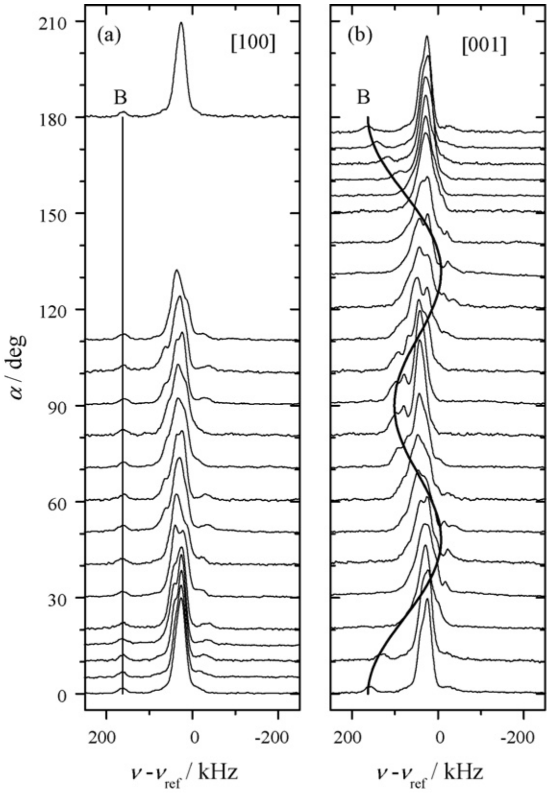

Fig. 2. Angular dependence of the ^{27}Al NMR central transition signal of a single-crystal of Co_4Al_{13}, for rotation around the (a) [1 0 0] axis and the (b) [0 0 1] axis, in the magnetic field $B_0 = 11.74$ T. Solid lines represent simulations of the resonance frequency as a function of angle of rotation α, using $\nu_Q = 4.0$ MHz, $\eta = 0$ and $\delta_{iso} = 780$ ppm.

4. Conclusions

The obtained form of electric field gradient tensor and its orientation of the largest principal axis parallel to [1 0 0] is in agreement with Wyckoff position (2*a*) lying on a (1 0 0) mirror plane. Moreover, from the intensity ratio of the NMR lineshapes it is possible to estimate that this corresponds to approximately four Al atoms per unit cell, being in agreement with the occupation of two sites with Wyckoff positions 2*a* by Al, as observed in the crystal structure. Altogether, the additional signal (B) corresponds to ^{27}Al nuclei with exceptionally large almost axially symmetric quadrupole coupling and high value of isotropic shift. This strongly supports the model of a unique bonding situation of Al in nearly linear Co–Al–Co molecular groups formed in Co_4Al_{13}.

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